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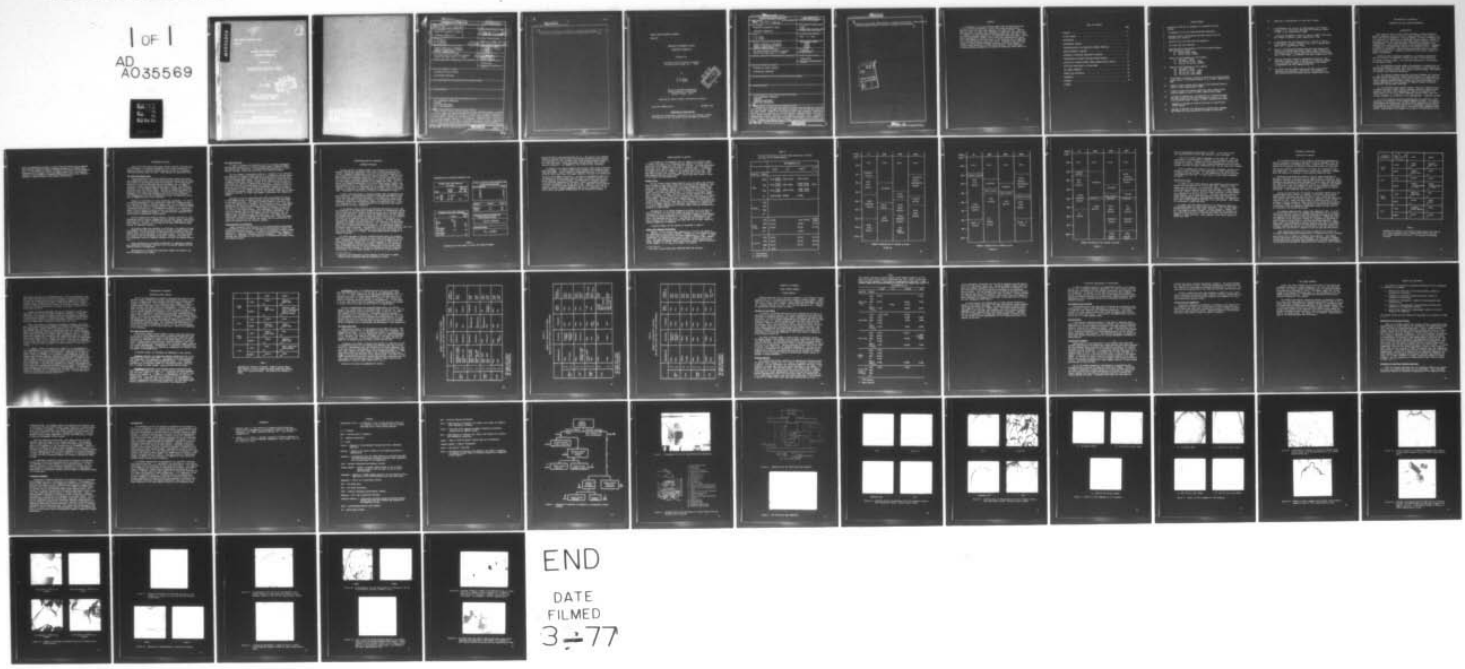

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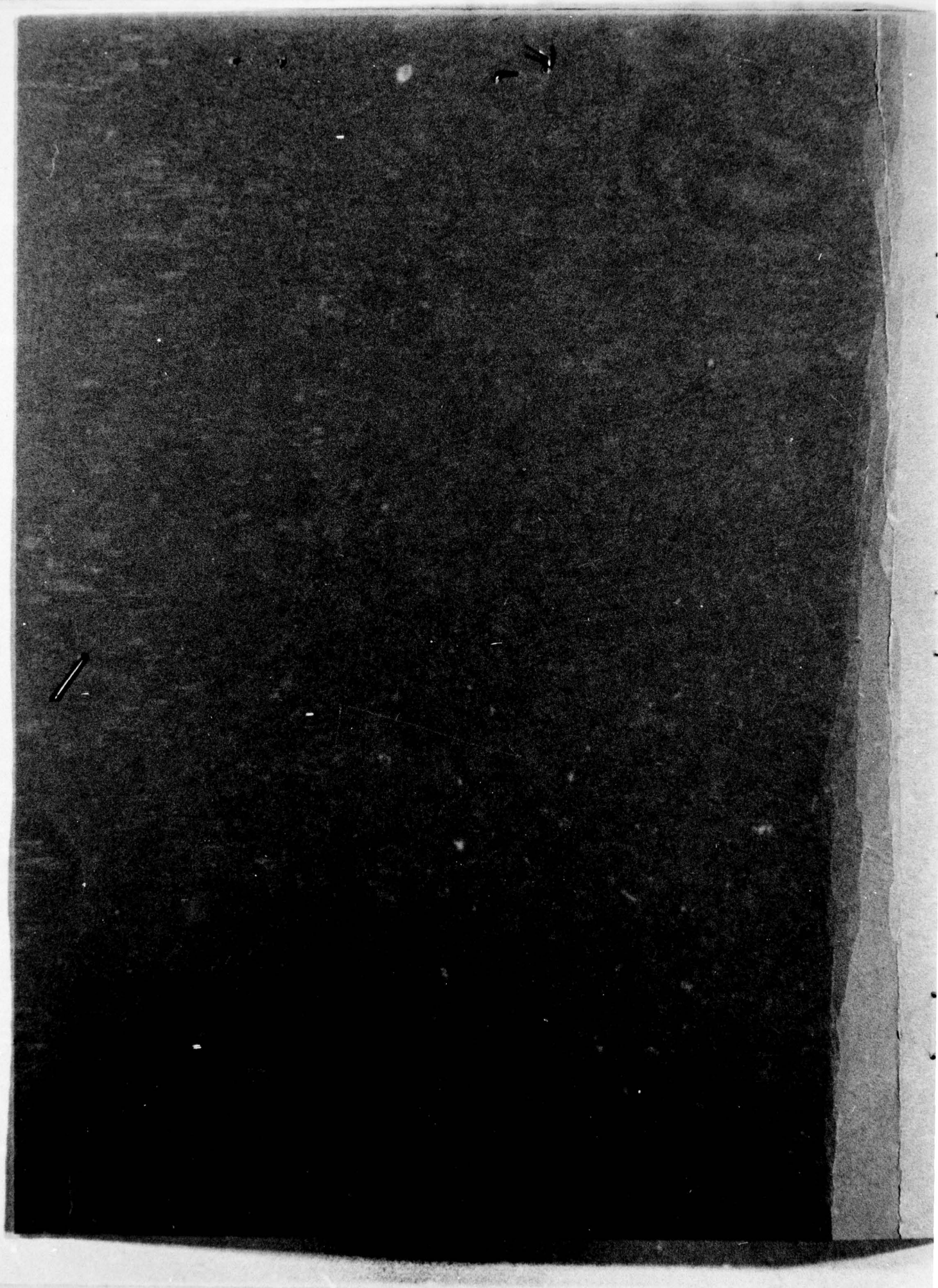

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BEHAVIOR OF ALUMINUM IN SOLID PROPELLANT COMBUSTION

Prepared for

Air Force Office of Scientific Research
Bolling Air Force Base, D. C. 20332

by

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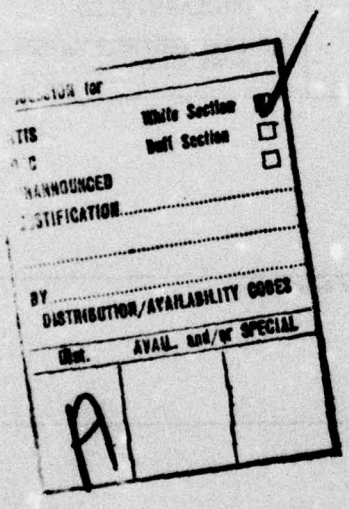

ABSTRACT

The behavior of various aluminum powders was observed during heating in controlled environments, using a hot stage microscope and a specially built hot plate drop apparatus (for rapid heating). Results show the effect of powder type, atmosphere, temperature, and binder type on formation of interconnected and coalesced particles, and help to clarify similar processes operative in the propellant combustion zone. Coalescence (agglomeration) tended to occur above the aluminum melting point, with the breakdown of the oxide shell on the particles (due to expansion of the melting aluminum) being a key factor. Conditions that inhibited contact of molten aluminum between particles inhibited coalescence, but usually caused particles to become interconnected. These conditions included oxidizing atmosphere or presence of propellant binder materials.

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THE BEHAVIOR OF ALUMINUM IN

COMBUSTION OF SOLID ROCKET PROPELLANTS

INTRODUCTION

When used as a fuel in solid rocket propellants, powdered aluminum exhibits combustion behavior that is in sharp contrast to the behavior of binder and oxidizer materials. Being an element, it doesn't decompose, and it is reluctant to vaporize at the propellant burning surface. Instead, it accumulates, melts, and coalesces into large droplets referred to here as "agglomerates". During these processes, ignition is suppressed by the formation of an oxide diffusion barrier on all exposed surfaces. Depending on conditions, the aluminum may follow any of the paths in Fig. 1 leading eventually to combustion. Because of the statistical nature of the propellant microstructure, a variety of behavior is seen during burning of a sample of propellant.

Unlike the other propellant ingredients, the aluminum agglomerates burn as a cloud in the combustion volume, and form a liquid (Al_2O_3) as the primary reaction product. The practical importance of the situation at this point is that

a) The propellant burning surface is populated by a complex array of interacting aluminum particles, which affects diffusion, heat transfer and heat release, to modify burning rate, erosive burning response, and response to transient flow (combustor stability).

b) The original aluminum particles have been converted into relatively large burning droplets with typical burning times of the same order as the stay time in the combustor; this leads to risk of poor combustion efficiency, possible unwanted dynamic coupling with flow disturbances, and a critical dependence of these processes on combustor design, propellant formulation, and operating conditions.

c) The condensed phase reaction product cloud is an important factor in nozzle efficiency, nozzle erosion, combustor stability, exhaust plume visibility and launch area contamination: these in turn depend on the characteristics of the Al_2O_3 cloud (especially particle size), which are strongly dependent on the details of the agglomeration - combustion process.

It is the foregoing practical considerations that lead one to focus attention on the details of the aluminum combustion process. The present investigation has started with the nature of the aluminum and its behavior during heating to temperatures typical of the propellant burning surface. Increasing attention is being given to the role of other propellant ingredients. These studies will progress to the point of clarification of the

nature of agglomerate droplets, at which time the studies can be combined with extensive available results regarding combustion of aluminum droplets. In the process, the effect of combustor gas flow on the intermediate processes will be studied, and the aggregate results will be interpreted relative to the problems of combustion efficiency, burning rate, combustor stability, nozzle efficiency, and exhaust plume effects.

EXPERIMENTAL METHODS

Most of the work during this report period involved controlled heating of samples, in controlled atmospheres, with visual observation of response, either by optical microscope during the test or by scanning electron microscopy after the test. These methods are described below:

Hot Stage Microscope Tests

Visual observation of particle behavior during subignition heating was accomplished using a Leitz 1350 water-cooled microscope heating stage and a Bausch & Lomb Dynazoom Laboratory Microscope. The heating stage is attached to the microscope stage and the microscope body is raised by inserting a spacer ring between the body and the stand. The sample is heated on a 7.5 mm diameter sapphire disk which is supported on a heater cartridge within the heating stage. The heating chamber and sample are sealed by clear quartz cover plates. Heating can be performed in an air atmosphere, or a controlled atmosphere (O_2 or Ar) may be introduced. The atmosphere gas flow rate is adjusted by Whitey micrometering valves with an immediate switch in gas available.

Heating is controlled by a Leitz regulating transformer. By continuous manual adjustment of the transformer to maintain a maximum current, it is possible to obtain a 28°C/sec heating rate. At the maximum heating rate, the melting temp of aluminum (660°C) is reached in 27 sec and 1000°C is reached in about 44 sec. A thermocouple, mounted in the heater cartridge below the sapphire specimen carrier, is connected to a galvanometer giving a direct temperature reading. Transmitted and/or reflected light can be used for observation during heating.

The test apparatus is shown in Figure 2, showing, from left to right, atmospheric control valves, transmitted light control, Bausch & Lomb microscope and Leitz hot stage, reflected light source, transformer and temperature read out. Figure 3 is a cut away of the Leitz 1350 heating stage showing the important features.

The heating stage test procedure is as follows: The sample is spread on a sapphire disk and carefully placed on the carrier support within the heating stage. The cover plate is inserted and the control gas flow and cooling water flow are adjusted to the correct levels. The light sources are turned on and the microscope is focused. Heating is initiated and the transformer control is manually adjusted to obtain the desired heating rate.

Visual observation, interrupted occasionally by temperature readings and transformer adjustments, continues until the desired temperature-time heating history is accomplished.

Observations are recorded and significant samples are taken to the SEM for preparation and viewing.

Hot Plate Drop Test

In order to overcome the relatively slow (by propellant standards) heating rates obtainable in the Leitz heating stage, a separate chamber was designed and constructed. This new apparatus incorporates the Leitz heating cartridge, regulating transformer, and temperature gauge.

The test chamber, illustrated in Figure 4, consists of two concentric stainless steel cylinders welded together by a cylindrical drop arm sleeve. The cylinders are capped by stainless steel plates which are bolted down to form a cooling water jacket. The top plate contains a vision port with a sapphire window which permits viewing of the sample carrier as well as easy access for removal of samples after each test. The bottom plate contains the leads for the heater power and thermocouple readout, as well as gas ports for introducing a protective atmosphere. Samples are placed in a cup drilled in a 1/4" diameter rod which is inserted through a fitting in the drop arm sleeve. Figure 5 shows the HPD rig with (from left to right), atmosphere controls, hot plate drop chamber, transformer, and temperature readout.

Operation of the hot plate drop test (HPD) rig proceeds as follows. A clean sapphire disk is lowered through the open vision port and placed on the heater cartridge. The sample (Aluminum powder) is placed in the cup and the sample arm is inserted 1" into the drop arm part. (The sample experiences the protective atmosphere during heating but is shielded from the heat by the cooling water.) Cooling water is started, the gas flow is turned on, and heating begins. The transformer is adjusted manually until the sapphire disk is stabilized at the desired temperature. The sample arm is extended into the chamber until it is directly over the sapphire disk, as viewed through the vision port. The sample arm is rotated 180°, dropping the sample onto the heated disk. After the sample cools down, the gas is turned off, the vision port is unscrewed and the sample and sapphire disk are carefully removed.

Characteristics of SEM Method

Sample preparation and operation of the scanning electron microscope is performed by the staff of the Physical Sciences division, Georgia Tech Engineering Experiment Station. The samples are generally coated by vacuum deposition of carbon followed by a coating of gold-palladium. Samples are analyzed in a Cambridge Stereoscan SEM for morphology. Some elemental analyses were performed by X-ray dispersion to differentiate between binder and aluminum residue.

CHARACTERIZATION OF AS-RECEIVED

ALUMINUM PARTICLES

Several sources of aluminum powder were solicited for this work. However, testing was restricted to four types, chosen because they were in use in commercial propellants, were also being studied elsewhere, or were of particular interest because of singular properties. The four samples studied were designated Alcoa 123, H-30, H-95, and a modified H-30. The Alcoa 123 is a standard classification of Aluminum Company of America, the test sample having been supplied by the company for study. The "H" series are standard designations of the Valley Metallurgical Company, and were obtained from Dr. K. Kraeutle of the U. S. Naval Weapons Center. The modified H-30 was from the same sample as the standard H-30, but had been treated (by Kraeutle) to increase the extent of oxide coating on the particles. The supplier's data sheet on Alcoa 123 is reproduced in Table 1.

To date, characterization of aluminum powders used in propellants has been superficial. Specifications applied in propellant manufacture cover little more than mean particle size and % total impurities. This is very likely not sufficient in some applications. Full characterization would presumably involve size distribution, details of impurities (e.g., % silicon, % magnesium, etc.). Characterization of the oxide skin may involve properties not yet fully recognized.

In the present study, attention was directed particularly at the visible properties of the oxide skin, primarily because the observational method used in tests was visual (optical microscope during tests, scanning electron miscroscope post-test). Figure 6a shows the appearance of the four samples of aluminum tested, and Figure 6b shows the surface quality of the particles. The Alcoa 123 is classified as -325 mesh aluminum by the supplier, is of very irregular shape, with relatively smooth surface. The mass-average "diameter" is probably around 20 microns.* H-30 consists of potato-shaped particles more nearly spherical than Alcoa 123. The surface is smooth-to-grainy, with occasional wart-like protrusions. The mass-average diameter is probably about 30 microns. The modified H-30 is not visibly different than H-30. The H-95 is seen to have large numbers of the wart-like protrusions and a very grainy surface on a 5 μscale. The mass-average particle diameter is roughly 95 microns.

An effort was made to find out something further about the aluminum particles by treatment in hydrochloric acid, using H-30, modified H-30 and H-95. Treatment of H-30 particles for 10 min. in 10% HCl-water solution produced very little effect (Fig. 7), while treatment in 100% HCl for 10 min. caused extensive change in the surface (features not yet explained). Tests on modified H-30 (at 10% only) produced very little visible effect. Treatment of H-95 aluminum in 10% HCl for 10 minutes produced relatively little effect (Fig. 8), while treatment in 50% HCl for 5 minutes led to

---

* Definition and measurement of mean diameter of particles is compromised by their irregular shape and variability in size.

PROPERTIES OF ATOMIZED POWDER NO. 123

SCREEN ANALYSIS, PERCENT (U. S. Std.)			
		Spec. for Shipment	
Mesh	Typical Range	Min.	Max.
+200	0 - Trace		0.2
-200 +325	1 - 10		
-325	90 - 99+	90	

TYPICAL PARTICLE SIZE DISTRIBUTION (Sharples Micromerograph)	
Wt. % Undersize	Micron
90	49
80	42
50	29
20	18
0	4

DENSITY	gmc/cc	lb/cu ft
Apparent	1.1	69
Tapped	1.4	88

CHEMICAL ANALYSIS, PERCENT		
		Limits
	Typical	Max.
Al	99.0	
Al_2O_3	.65	
Fe	.15	.25
Si	.07	.15
Other Metallics, Each	.01	.03
Other Metallics, Total	-	.15

AVERAGE PARTICLE DIAMETER (Fisher Sub-Sieve Sizer)
APD 15 - 19 Microns

SURFACE AREA
.20 - .30 M^2/G

TABLE 1

Manufacturer's Data Sheet on Alcoa 123 Aluminum Powder.

massive attack on the particles (Fig. 8c, d). The nature of the residual particles suggests that the oxide film has been protective over portions of the surface, but that isolated local flaws permitted massive attack by HCl from those sites. These exploratory results suggest that further testing is merited -- for example on H-95 in 20% HCl for 10 minutes.

In summary, the aluminum samples each contain a wide range of particle sizes and shapes. All have a rather grainy surface, with occasional wart-like protrusions. Purity claims by the manufacturers are in the vicinity of 99.3%, with Al_2O_3 being the largest impurity, iron next and silicon next (based on Alcoa sample literature). The oxide is presumably primarily on the exterior of the particles, would be about 0.5 microns thick on a 30 micron particle if so distributed. The oxide skin is generally believed to be relatively impervious to diffusion. Under the extremely adverse conditions of immersion in 10% HCl for 10 min., relatively little reaction occurred. Under more severe conditions of 50 - 100% HCl, there was extensive attack in a manner suggesting local sites of penetration of the oxide rather than general deterioration of the "protective" quality.

BINDER RESPONSE TO HEATING

In anticipation of subsequent tests of samples with aluminum powder in binder, tests were run to determine what response to heating could be attributed to processes other than those of aluminum. Hot stage microscope tests were run on samples of pure binder,* of binder with 16.7% ammonium perchlorate (AP), and of binder with 16.7% aluminum oxide. In all cases, the binder was cured as a puddle on the sapphire disc of the HSM. Tests were made in Argon, and in Oxygen. Heating time was around 5 min., and peak temperatures were usually 1000°C. Actual tests were listed in Table 2, and results are discussed below.

Binders Alone

All the binders tested behave similarly, with out-gasing and discoloration followed by some slight motion due to distortion and shrinking. Bubbling activity becomes boiling which (in Argon atmosphere) rapidly dissipates much of the sample, leaving a solid-looking film of residue, brown or black. This state was reached by a P.S. binder at 320°C, by PBAA at 500°C, CTPB at 520°C and HTPB at 540°C. The boiling is extremely vigorous with PS and HTPB. For PBAA, CTPB and HTPB, further changes up to 1000°C amount to shrinking or cracking of the residue film, with much of it remaining at 1000°C. PS binder (in Argon) experienced a boiling decomposition at 340°C which rapidly reduced it to a black residue. The most notable differences among the binders tested were the low temperature of decomposition of PS, its flaming reaction, and relatively large amount of residue; and the slightly lower temperature of the PBAA primary (boiling) decomposition compared to CTPB and HTPB.

Decomposition in an oxygen atmosphere is similar up to the point of onset of boiling. At this point sudden ignition may occur with rapid consumption of the volatile portion of the sample, leaving a black residue. This ignition behavior appeared to be erratic as to temperature of occurrence, and sometimes did not occur. Non-ignition was no doubt in part due to tendency for the sample to pull away from the hot plate, where the reported temperature is measured.

A general summary of test results is presented in Table 3.

Binder with Ammonium Perchlorate

Samples of four binders were prepared with 16.7% AP, and tested in the same manner as pure binder samples. Presence of the AP caused increased out-gasing and discoloration at the lower temperatures $T < 300°C$. In argon atmospheres, the vigorous boiling phase occured at somewhat lower temperature. The usual stable black residue occurred. A switch from Argon to Oxygen atmosphere at 1000°C lead to ignition and nearly complete combustion of the residue. In the case of PS binder, the vigorous

---

* The tests on pure binder were conducted under ONR contract.

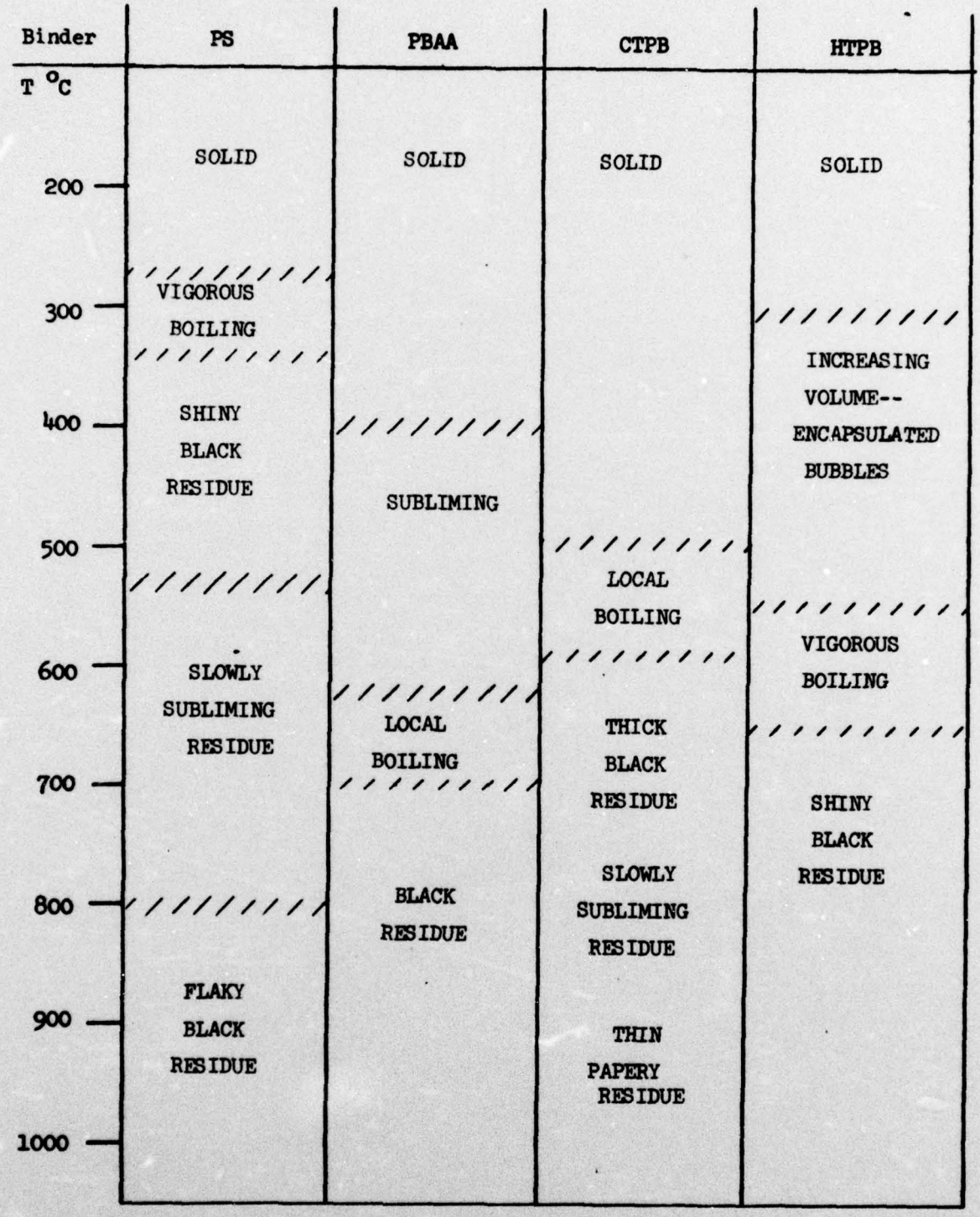
TABLE 2

Listing of Tests Run in the Hot Stage Microscope on Binders and Al_2O_3 and AP-loaded Binders.

		ENVIRONMENTAL GAS			
		Argon*	Air*	Oxygen*	Air**
ADDITIVE	BINDER				
NONE	HTPB	6/73W 14/87W 13/87W	2/85W 16/87Y	1/84Y 25/88Y	
	CTPB	1/42W 23/88Y 11/86Y	6/85Y 9/86W	15/87W 24/38Y 9/44Y 12/86Y	8/44Y
	PBAA	1/58Y 7/86W 10/86Y	8/86W 17/87Y	5/85Y 4/85Y 3/59W 18/87Y	
	PS	1/39W 22/88W	20/88W	21/88W	
2% Fe_2O_3	HTPB				
	CTPB				
	PBAA				
	PS				
16.7% Al_2O_3	HTPB	11/74W		9/44Y 20/76W	13/74Y 8/44Y
	CTPB	16/71Y		18/72W	17/71Y
	PBAA	16/72W		18/72Y	17/72Y
	PS			6/41Y	
16.7% AP	HTPB	12/74Y		21/76W	14/74Y
	CTPB	19/77W		21/77W	20/77W
	PBAA	19/77Y		21/77Y	20/77Y
	PS	7/42W			

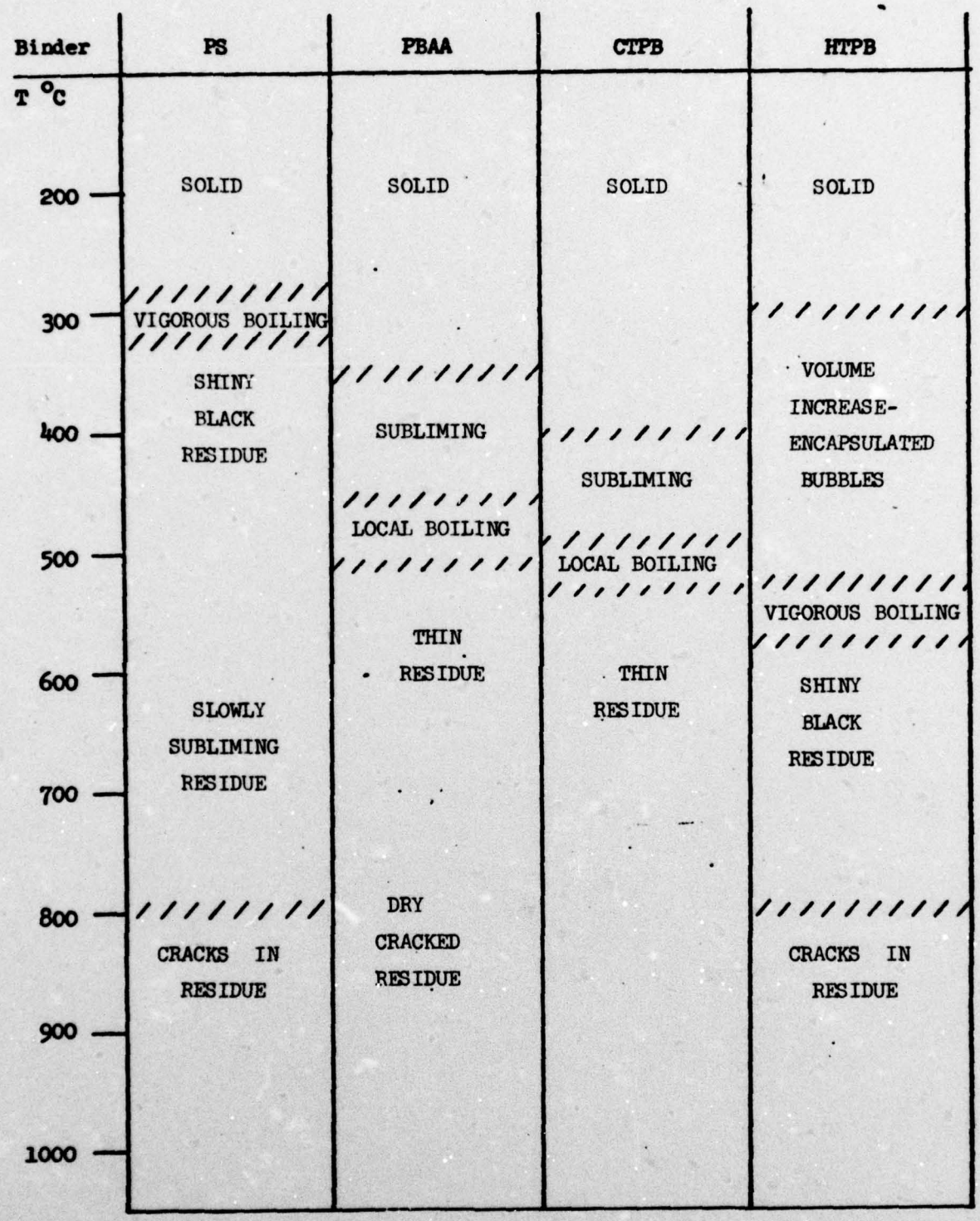
* Slow Heating

** Rapid Heating



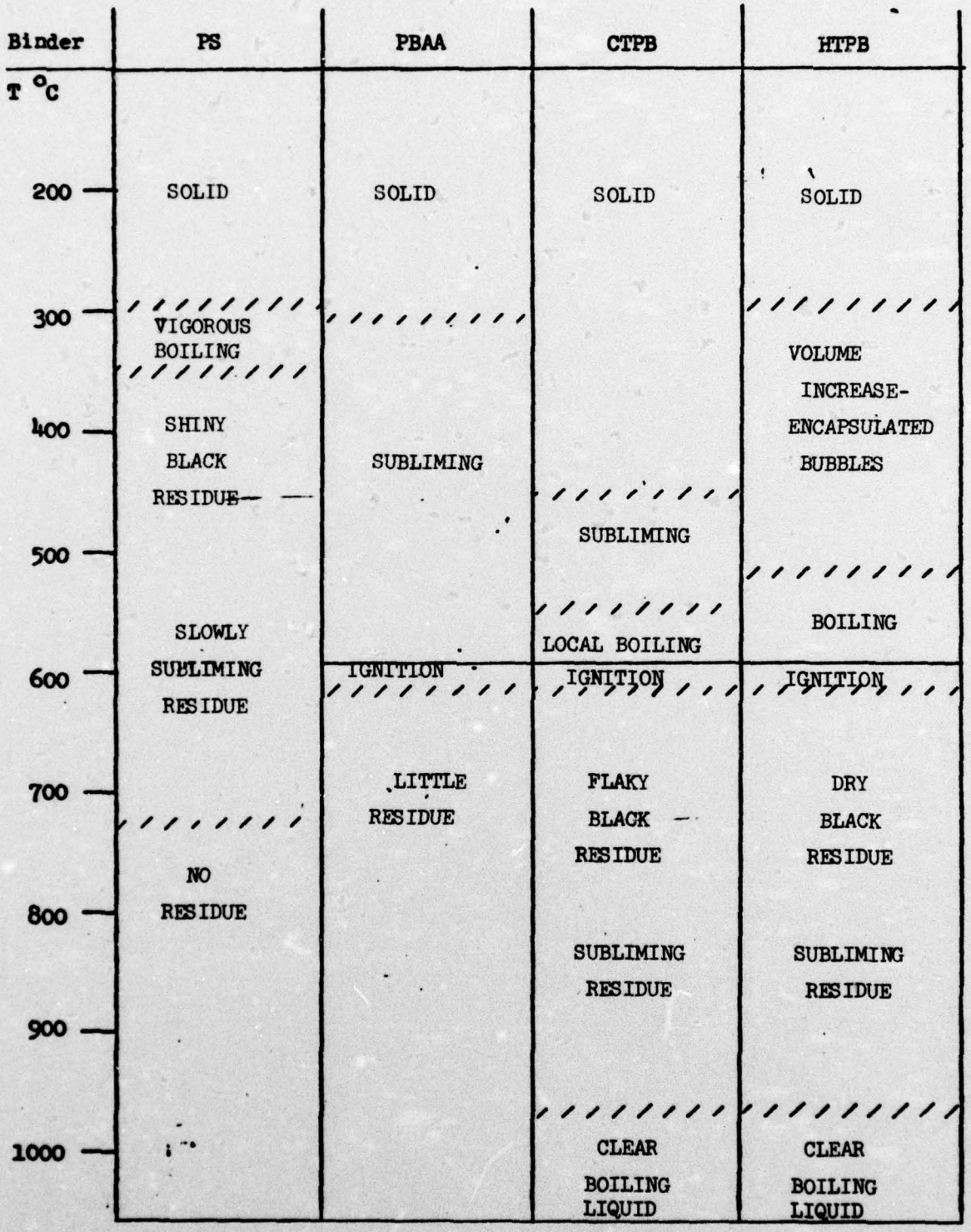
THERMAL DECOMPOSITION OF BINDERS IN ARGON

FIGURE 3a



THERMAL DECOMPOSITION OF BINDERS IN AIR

FIGURE 3b



THERMAL DECOMPOSITION OF BINDERS IN OXYGEN

FIGURE 3c

phase of decomposition was finished at 350°C. In the case of HTPB, the vigorous boiling at 450°C was replaced by rapid shrinkage.

Since the AP would normally decompose in the range 220 - 400°C in these tests, one would expect out-gasing to be increased at these temperatures as it was. The amount of AP was apparently not sufficient to dominate the behavior, and the more vigorous decomposition of the binder normally occurring at higher temperatures was thus not drastically changed.

When the samples were tested in an Oxygen atmosphere, behavior was similar to that in Argon up to the temperature at which rapid boiling or smoking occurred in Argon. At that temperature, abrupt ignition and rapid combustion occurred. In these tests, no black residue remained at 1000°C.

Binders with Al_2O_3

In order to study binder behavior when loaded with solid particles, samples were prepared with 16.7% Al_2O_3 particles. Response of these samples was very similar to the pure binder samples. At those temperatures where boiling behavior occurred with the binder, the same happened with Al_2O_3 present, and the resulting remnant retained a cratered appearance produced by the boiling activity. The oxide retained a coating of binder residue, and in areas where particles were close together, the particulate assemblage was a connected mass of material, at temperatures below that at which aluminum would melt if it were present. This condition persisted to 1000°C and above.

In oxygen, the PBAA sample ignited at the temperature where the corresponding sample in Argon boiled vigorously. CTPB and HTPB samples behaved similarly to the Argon tests, without ignition. However with all three samples tested in oxygen, the black residue was reduced, the Al_2O_3 particles were white (a few dark with HTPB), and there was less adhesion of oxide particles. There remained a dark liquid residue at 1000°C with HTPB.

RESPONSE OF INDIVIDUAL

PARTICLES TO HEATING

It is believed that much of the aluminum accumulation-agglomeration behavior observed in propellant combustion is due to response of the individual particles as the temperature rises. Specifically, the thermal expansion of the aluminum is expected to deform and/or flaw the Al_2O_3 skin and extrude aluminum to the exterior of the skin, even draining it under some conditions. This detailed behavior contributes to adhesion, agglomeration and ignition of aluminum in the propellant combustion zone.

Response of particles was studied in the hot stage microscope, by placing a collection of particles on the sapphire plate of the HSM in random manner referred to as sparse packing (some particles touched each other). Temperature and atmosphere were programmed in various ways, and observations were made of behavior during heating and cooling. In addition, some samples were subjected to post-test examination with an SEM, primarily because of limitations in resolution and depth of field in viewing with the optical microscope. (Test conditions and results in Table 4.)

Heating of particles of H-30 produces no noticeable results until the aluminum melting point (660°C) is reached. At this point the particles expand visibly, and some jump from the field of view. Particles that are near together tend to form strings (Figure 9), especially as the temperature continues to rise. Aside from some change in reflective quality of the surface, no further changes in single particles are visible during heating to 1000°C, followed by cooling. Contraction is visible during "freezing." Unfortunately there is apparently considerable surface activity that is not resolved in the optical microscope.

The samples remaining after cooling were examined by SEM. It is observed that particles tend to be somewhat more spherical (on the average) than before heating, suggesting that the oxide skin accomodates for aluminum expansion during melting by deformation-inflation. Cooled particles are observed to have large warts (Figure 10), suggesting of extrusion of molten aluminum through flaws in the oxide skin during expansion. Such warts usually are accompanied by parent particles that have a "collapsed" appearance, suggesting that the extruded aluminum solidified first during cooling, requiring contraction of the oxide skin of the main particle to accomodate for contraction of aluminum in both the wart and the particle.

These observations support what would be expected on the basis of the known thermal expansion characteristics of aluminum and Al_2O_3, including particularly the 6% volumetric expansion during melting. They suggest further conclusions that are less predictable. The occurrence of jumping of particles at the Al melting point suggests that the oxide is experiencing discontinuous deformation, suggesting either cracking or other inelastic

Aluminum Designation	Peak Temp. ↓ / Gas →	Argon	Oxygen
Alcoa 123	750°C	Trace, small 21	Moderate - small size 27
	1000°C	Slight, small size 23	Slight 29
H-30	750°C	Chains 1	Chains 7
	1000°C	Chains, chains formed at 700°C 3	Chains, chains formed at 700°C 9
Modif. H-30	750°C	Moderate-small size 31	None 37
	1000°C	Chains 33	Slight chain 39
H-95	750°C	Clumping, slight agglom. 11	Slight 17
	1000°C	Chains 13	Slight 19

TABLE 4

Agglomeration Behavior of Dispersed Aluminum Powder Upon Heating in the Hot Stage Microscope. (Roughly 50% of particles were near enough together to interact). See glossary for meaning of words.

deformation (perhaps during spheroidization). This is supported by real-time observation (above the Al M.P.) of abruptly shifting highlights from the particle surface during heating and cooling, suggestive of buckling behavior of an inelastic oxide skin. Adhesion of particles in contact suggests escape of aluminum and bridging at adjoining surfaces (Figure 11). Warting is a direct manifestation of escape of aluminum, evident at the single-particle level.

Escape of aluminum presumably can occur by diffusion through the oxide skin, and in other ways less visible than "warting". Kraeutle[1] observed that the escape of aluminum could be more decisively induced if the aluminum was heated on a platinum surface, presumably because molten aluminum "wets" platinum, and hence will exert a strong surface tension force that practically evacuates the oxide skin (Fig. 12).

Using this property to "amplify" the escape of aluminum, HSM tests were run on different aluminum samples in different atmospheres to different temperatures. Sample results are shown in Fig. 13. In general, it was observed that all types of Al tested would drain onto platinum wire. Fewer of the modified H-30 particles drained (Fig. 14), and the remaining oxide "bags" were evidently thicker (didn't collapse so fully). A similar result was obtained with standard Al when temperatures were only slightly above the Al melting point. Efforts were made to get SEM's of broken edges of the oxide "bags", but they appear to curl: it could only be concluded that they were less than 0.5 micrometers thick. The behavior of particles heated on platinum does not appear to be much different in Argon than in Oxygen.

In summary, effects of heating up to 1000°C or so are dominated by the transformation to liquid aluminum at 660°C, and the deformation of the Al_2O_3 skin due to expansion of the aluminum -- especially at its melting point. There is a tendency for the oxygen in the atmosphere to delay or prevent such physical response, because it oxidizes exposed aluminum and "heals" flaws in the oxide skin (forestalling ignition). Individual particles respond to heating and expansion by inflating the oxide skin, extrusion of aluminum to form wart-like protrusions, and sometimes by draining of the oxide skin. The oxide skin appears to be roughly 0.01 micrometers thick, with both thickness and detailed structure probably different according to details of the manufacture of the aluminum powder. The response to heating is dependent on the properties of the oxide skin, but very little attention has been given to characterizing the skin -- making generalizations or interpretations largely speculative.

INTERACTION OF ALUMINUM PARTICLES DURING HEATING

One of the mechanisms for cohesion of aluminum particles on a propellant burning surface that has been hypothesized is the direct interaction by bridging with molten aluminum that has leaked or diffused through the oxide skin. Such a bridge may either oxidize in place, or surface tension may simply cause the molten metal to coalesce into a larger droplet, referred to here as an agglomerate. In the present studies, this behavior was examined with the HSM for several types of aluminum, in several atmospheric situations, and at several temperatures. As in the case of samples of non-interacting particles, observations were made in real time, and in selected instances samples were examined subsequently in the optical microscope and the SEM. In addition, a test device was designed, built and used, that permitted samples to be dropped on a preheated sapphire plate, permitting heating times approaching those in the propellant combustion zone. Test conditions and observations by optical microscope are summarized in Table 5 for hot stage microscope tests, and in Table 6 for hot plate drop tests. Results are summarized in the following:

Hot Stage Microscope Tests

All aluminum powders tested tended to sinter under some conditions in the HSM, at some temperatures above the aluminum melting point; and some degree of agglomeration could be induced between 700°C and 1000°C. Sintering was evidenced by rigidity of the powder sample after heating; visible bridges between some particles could be discerned in post-test SEM's. Agglomeration was more obvious, since the powder sample coalesced into several agglomerates. Susceptibility to sintering or agglomeration was conspicuously dependent on temperature, atmosphere and original aluminum powder, as discussed below.

As general trends, the following are indicated by test results:

Sintering generally occurred among densely packed particles if the temperature was raised above 700°C. The degree of sintering increased with temperature, but progressed to agglomeration in a non-oxidizing atmosphere. The modified H-30 sintered less easily. Fig. 9 showed a sintered chain of particles formed in a low-packing density tests and Fig. 11 showed the oxide bridge. Al_2O_3 particles did not sinter.

Agglomeration generally occurred among densely packed particles above 750°C when oxygen was absent, while sintering and small agglomerates were more common in O_2 (Fig. 15). Agglomeration occurred to some degree in all samples at 1000°C in all atmospheres, but only to a limited extent in O_2, especially with samples of H-95 and samples of modified H-30. Conditions that favored occurrence of agglomerates also tended to agglomerate the sample more completely, and into larger agglomerates (conditions of low O_2 concentration, high temperature).

		Argon	Oxygen
Alcoa 123	750°C	Slight 22	Moderate - small size 28
	1000°C	Some, small size 24	Moderate, small size. Substantial agglom. at 680° during cooling 30
H-30	750°C	Slight 2	Trace 8
	1000°C	Massive, all sizes 4	Slight, small size 10
Modif. H-30	750°C	Slight, small size 32	None 38
	1000°C	Slight 34	Moderate, small size 39
H-95	750°C	None 12	None - particles spheroidized 18
	1000°C	Slight 14	Trace 20

TABLE 5

Agglomeration Behavior of Densely Packed Aluminum Powder Upon Heating in the Hot Stage Microscope (particles piled up about 2 to 3 particles deep). See glossary for meaning of words.

Agglomerates tend to be nonspherical and show their constituent particles when heated only to the low end of the agglomeration range (Fig. 16). At higher temperature the agglomerate spheroidizes (Fig. 17). The exterior surface no longer shows remnants of the oxide from the ingredient particles, but shows wrinkles or buckling of the surface indicative of aluminum contraction within a solid oxide skin. At this point it is not clear whether all the ingredient oxide has reached the surface, or whether there is an oxide structure within the agglomerates.

Etching of agglomerates was explored superficially, and results suggest that further study by this method might be instructive. Fig. 18 shows an agglomerate that was etched for 5 min. in 50% HCl. The oxide skin appears to have fared poorly. The exposed interior exhibits a pattern suggestive of crystalographic lines. Considering the fact that the agglomerate contained many ingredient aluminum particles, it is surprising that the etch lines are parallel over a large part of the agglomerate (suggesting that original oxide has migrated out of the interior during the period that the agglomerate was maintained at high temperature).

Hot Plate Drop Tests

Rapid-heating tests in the HPD apparatus were made on the four aluminum powders noted before, in atmospheres of Argon, Air and Oxygen. Two procedures were used. In one, the plate was brought to a temperature of 1000°C, and the heater shut off immediately after the sample was dropped. In this procedure, the temperature dropped at a rate such that 600° was reached in 50 seconds. In the second procedure the sample was held at 1000° for 60 seconds before the heater current was shut off.

In general, the trends in behavior were similar to those with the HSM. The modified H-30 and the H-95 aluminum agglomerated less than H-30 and Alcoa 123. Agglomeration was less extensive in an Oxygen atmosphere than in an Argon one, but connectedness of the particles was greater in Oxygen. Most tests yielded a few empty oxide shells (aluminum drained out). Sometimes shells were only partially empty, and a significant number were broken on one side and had warts on the opposite side. The tests in which 1000°C was maintained for 60 sec showed more particle interaction than the other tests, but the difference was not dramatic (maybe twice as much agglomeration, sintering, empty oxide shells, etc.).

Results of all tests are summarized in Table 6.

TABLE 6A

SUMMARY OF OBSERVATIONS OF SAMPLES

FROM HOT PLATE DROP TESTS IN ARGON ATMOSPHERES

		Agglomeration	Sintering	"Cracking"	Oxide Shells	Surface Appearance
Alcoa 123	S* H	Extensive, large, slightly irregular shape	Extensive	Slight	None	Rough Shiny
	L H	Extensive, very large	Extensive	None	Several	
H-30	S H	Extensive, med. size, irregular shape	Extensive	In Agglomerates	Fragments	Rough Dull
	L H	Extensive, med. size, regular	Extensive	In Agglomerates	Several	Rough Dull
Modif. H-30	S H	Some, small size	None	In Agglomerates	Two	Rough Dull
	L H	Some, small size	Extensive	None	Several + Fragments	Rough Dull
H-95	S H	None	None	Some	None	Rough Dull
	L H	None	Some, Chains	Some	One	Rough Dull

* "SH" means short heating
"LH" means long heating
See text for explanation.

TABLE 6B

SUMMARY OF OBSERVATIONS OF SAMPLES
FROM HOT PLATE DROP TESTS IN AIR ATMOSPHERES

		Agglomeration	Sintering	"Cracking"	Oxide Shells	Surface Appearance
Alcoa 123	S* H	None	Extensive, Clumped	None	Some	Shiny Smooth
	L H	One Large	Extensive, Clumped	None	Many	Rough Dull
H-30	S H	None	Extensive	None	None	Shiny Smooth
	L H	Moderate, small and med. size	Extensive	None	Many	Smooth Dull
Modif. H-30	S H	A few, small size	Some	None	A few	Rough Golden Brown
	L H	None	Some	None Warts	Many	Rough, Dull, Warts
H-95	S H	None	Slight	Some	Several Partial Empty - Wart Combination	Rough Dull
	L H	None	Slight	Some	Many Partial Empty - Wart Combination	Rough Dull

* "SH" means short heating
"LH" means long heating
See text for explanation.

TABLE 6C

SUMMARY OF OBSERVATIONS OF SAMPLES

FROM HOT PLATE DROP TESTS IN OXYGEN ATMOSPHERES

		Agglomeration	Sintering	"Cracking"	Oxide Shells	Surface Appearance
Alcoa 123	S* H	None	Extensive, Chains	Slight	None	Rough Shiny
	L H	None	Extensive, Chains	Slight	Two	Rough Dull
H-30	S H	Slight	Slight	None	None	Scaly Shiny
	L H	Slight	Slight	Slight	Few	Rough Dull
Modif. H-30	S H	None	None	None	One	Rough Dull
	L H	Slight	None	None	Few	Rough Dull Warts
H-95	S H	Slight	Slight	Some	None	Rough Dull
	L H	None	None	Some	Two	Very Rough, Grey

* "SH" means short heating
"LH" means long heating
See text for explanation.

BEHAVIOR OF ALUMINUM - LOADED BINDER SAMPLES DURING HEATING

Heating tests were run in the HSM on samples of four different binders prepared with 16.7% of several different grades of aluminum powder. Tests were all of about 3 minute duration, with temperature programmed to 1000°C, with tests in Argon and in Oxygen. Binders used were HTPB, CTPB, PBAA and PS. Aluminum used was Alcoa 123, H-30, H-95 and modified H-30. A summary of combinations tested is given in Table 7.

Behavior of the Binder

In general, the binder behaved as if the Aluminum were not there, as described in a previous section. All binders exhibited a melt-like state far below the aluminum melting point (AlMP), preceded and followed by gassification. All but PS binder decomposed and out-gassed most of their mass below the AlMP. P.S. binder yielded an extensive black solid mass that survived to 1000°C in both Argon and Oxygen. The other binders, after out-gassing, left a thin dark film on the test plate and on all the particles, usually producing a connective structure between particles. The overall assemblage was often nonuniformly distributed on the test plate because of bubbling of the binder during gassification, and because of shrinkage of the connected assemblage in the latter stage of heating and during cooling (Figure 19).

The tests in Oxygen tended to yield erratic or deceptive results. The sample tended to lose contact with the heater plate where the temperature was measured. The indicated temperature for onset of rapid gassification of the binder was erratically higher in Oxygen atmospheres, a result that may not be significant. Ignition occurred in about half of the tests in oxygen, over a wide range of indicated temperatures. The fact of ignition in O_2 atmospheres is significant; but values of indicated ignition temperature or even the occurrence-nonoccurrence of ignition vs. binder, probably are not meaningful because of uncontrolled thermal contact of samples in oxygen atmosphere.

Aluminum Behavior

The aluminum was clearly visible in the samples well before reaching its melting point (except with P.S. binder), but showed no activity until it melted. At that temperature the inevitable expansion occurred; further response to heating was gradual and varied according to test sample. Considering only HTPB, CTPB and PBAA binders, H-95 aluminum did not agglomerate in any tests (excluding those where ignition occurred). Modified H-30 showed only slight agglomeration, while H-30 and Alcoa 123 showed moderate agglomeration (30% of the particles formed into agglomerates of 2 or 3 times larger diameter than the original particles). The atmospheric gas did not affect this result much when ignition did not occur. A

TABLE 7

Test Numbers Indicating Aluminum-Loaded Binder Samples Tested in the Hot Stage Microscope (the notation 10/80W means test #10, listed on white page #80 of the lab notebook). "Slow heating" is described in the text. "Fast heating" means the HSM was preheated to 1000°C and the sample then introduced.

		ENVIRONMENTAL GAS			
		Argon*	Air*	Oxygen*	Air**
ADDITIVE	BINDER				
	HTPB	10/74W			9/76W
	CTPB				
Alcoa 123 Alum.	PBAA	13/63W		15/63Y	9/61W
	PS		5/41W	6/41Y	
	HTPB+ 2% Fe_2O_3	4/78Y		12/80W	8/79Y
	HTPB	7/73W 1/78W		16/75W	
	CTPB	2/42Y		4/43W	3/43W
H-30 Alum.	PBAA	4/59W		6/60W	5/60W
	PS	2/39Y			
	HTPB+ 2% Fe_2O_3	1/78W		9/79Y	5/79W
	HTPB	9/73Y		18/75Y	
	CTPB	10/45Y			4/65W 11/45Y
H-95 Alum.	PBAA	12/62Y		14/63W	8/60Y
	PS	4/40W			
	HTPB+ 2% Fe_2O_3	3/78Y		11/80W	7/79W
	HTPB	8/73Y			
	CTPB	5/43Y			
Modif. H-30	PBAA	10/61W			
	PS	5/43Y			
	HTPB+ 2% Fe_2O_3	2/78W		10/80W	6/79W
	HTPB	1/78W		5/79W	
16.7% H-30 Alum. + 2% Fe_2O_3	CTPB				
	PBAA				
	PS				

* Slow Heating

** Rapid Heating

curious phenomenon illustrative of the flow of aluminum occurred particularly with CTPB binder (Figure 20). Recovered samples showed streaks and spires of aluminum, apparently drawn out of particles by adhesion to the test plate and/or other particles due to shrinkage of the assemblage during cooling. This was observed with both H-30 and modified H-30 aluminum, and was seen also (less frequently) with PS binder. Further evidence of aluminum flow is seen in Figure 21, which shows a post-test sample of CTPB + Modified H-30 aluminum in which many of the particles have drained and left transparent oxide shells.

As noted earlier, the samples with PS binder behaved differently because of the large fraction of the binder surviving the primary gassification and the heating to 1000°C. The aluminum behavior became visible only gradually in the 700 - 1000°C range. The binder-coated particles appeared to crack and leak fresh aluminum onto their surfaces, giving a partially shiny, partially dull black surface on particles. Agglomeration of the aluminum in PS binder was rather limited, although it was the only binder in which agglomeration of H-95 Aluminum occurred in the absence of ignition.

ACTIVITIES PRELIMINARY TO FUTURE WORK

In order to produce results in an experimental program, it is necessary not only to establish suitable techniques, but also to refine and standardize such techniques until they produce consistently high yields of useful information. In pursuit of this goal, much of the effort expended during the past year has been in the area of developing and refining experimental techniques involving both the previously reported particle heating experiments, and the proposed combustion of aluminized propellants with ordered structure.

High Speed Motion Pictures

Several movies have been made using the Georgia Tech combustion photography system in order to gain experience in the use of this equipment and to establish proper exposures for aluminized propellants. This system consists of a high pressure window bomb, Hycam high-speed motion picture camera, and Xenon light source. This facility was modeled after the facility at the U. S. Naval Weapons Center.

Quench-Burning

A high pressure combustor similar to that used in combustion photography was used for interrupted burning of samples, which were subsequently examined with a scanning electron microscope. The same combustor was also used as a collector for combustion residue. These techniques were used to check out their suitability for forthcoming work. It was found that quenching of aluminized propellants by rapid depressurization was not reliable except from fairly high pressures. Some combination method is proposed for tests under adverse conditions, such as cold gas impingement following depressurization.

Pressed AP-Al Samples

Samples made by dry pressing AP-Al or AP-Al-binder mixes have been prepared representing both conventional random packings and ordered packings. One inch diameter disks containing AP-Al mixtures are made by dry pressing the ground AP and as-received Al in a specially prepared mold in a Carver hydraulic press at 27,000 psi. A technique has also been developed for dry pressing large AP (125μ) with fine aluminum (20μ) which overcomes the tendency of the fine Al to sift through the large Al leaving a non-uniform sample. A vaporizer is used to raise the relative humidity in the preparation area so that the surface of the AP becomes sticky enough to hold the find Al. Microscopic examination of these samples reveals a uniform random distribution of the AP-Al mix.

One of the shapes proposed for investigation of propellants with ordered structure consists of compacted concentric cylinders. These will be formed by preparing a pressed annular AP or AP/Al cylinder and filling the center section with various combinations of Al/binder or pressed Al. Several methods have been used for pressing AP annular cylinders with varying degrees of success. Stainless steel molds have been made for

pressing both solid cylinders and annular cylinders. The solid cylinders are then drilled out by hand. While both methods have produced satisfactory samples, the percentage of successful preparations is quite low. New molds are being designed which will hopefully overcome these difficulties.

Annular cylinders have also been prepared by packing AP into rubber tubing, plugging the ends with rubber stoppers, inserting needles down the axis of the tubing and iso-statically pressing this assembly in an Autoclave Engineering Isostatic Press.

Scribed Dies for Sandwiches

Propellant sandwiches are prepared by spreading a thin layer of binder between two AP slabs, the AP slabs being cut from pressed AP disks. Special molds have been built incorporating scribed or ribbed dies which are used to press grooved AP disks. Sandwiches made with these grooved disks will have ordered columns of binder or binder/Al.

THE JANNAF WORKSHOP

During this year a workshop on the title topic of this report was organized, chaired and a report presented to the Joint Army-Navy-NASA-Air Force Inter Agency Propulsion Committee (at the Combustion Workshop Group Meeting on September 16, 1976). The summary report will be published by the Chemical Propulsion Agency in the proceedings of the 13th JANNAF Combustion Meeting. Organizing and reporting activities were partially supported by this project.

The Workshop discussions covered the behavior of aluminum in laboratory tests, and those aspects of combustion zone behavior shown in Fig. 1. Widely divergent viewpoints were revealed regarding the mechanistic basis of aluminum particle adhesion-accumulation; it was generally agreed that too little was known even about the aluminum powder itself! However, concurrence was reached on many important points and the participants all gained in perspective and objectivity, many being stimulated to explore further the issues raised. For details of the Workshop, reference may be made to the above-mentioned CPIA Publication.

SUMMARY AND DISCUSSION

The behavior of aluminum in propellant combustion can be categorized in a sequence of processes

1. Retention of particles on the burning surface, leading to accumulation in quantity.
2. Breakdown of individual aluminum particles, leading to interaction of particles.
3. Formation of "accumulates", masses of interconnected aluminum particles.
4. Formation of "agglomerates", large droplets resulting from coalescence of accumulated particles.
5. Ignition and combustion of agglomerates, mostly in the free volume of the combustor.

The present results are most effectively discussed in the context of items 1 - 4.

Retention on the Burning Surface

Tests on the binders showed that all went through a semi-molten stage during heating in either argon or air atmospheres, at temperatures around 100°C less than the aluminum melting point. Thus it seems reasonably certain that during propellant combustion, aluminum particles in the propellant (binder) will be reached by a burning surface that is wet, and will retain the particles by adhesion. This in turn permits the particles to be joined by underlying particles as the binder pyrolizes, providing for accumulation of aluminum in some complex pattern reflecting the original distribution of the aluminum in the propellant microstructure. The tests on binders showed significant differences in the temperature range above 550°C, with the amount of residue from the "boiling" phase being much greater for CTPB and HTPB binders than PS and PBAA binders. In oxygen atmospheres, HTPB and CTPB binders pyrolized to leave a clear liquid at 950°C, some of which survived to 1200°C and remained when that temperature was maintained. Thus some surface wetting by binder persists to quite high temperatures. Behavior to be expected in the propellant combustion zone would presumably be dependent on microscopic distance from oxidizer surfaces, but it seems reasonable to expect a persistent wetness of binder surfaces. This is consistent with observations of melt flow on burning surfaces (Ref. 2).

Breakdown of Individual Aluminum Particles

While the thermal wave moves into the propellant ahead of the combustion zone, the aluminum particles heat as individuals. Their subsequent interaction behavior is clarified by examination of the behavior of indi-

vidual particles. The present results are consistent with earlier ones in showing no notable visible change in particles until the melting point of the aluminum is reached. In a propellant combustion zone, this suggests that the aluminum particles behave primarily as heat sinks in the pyrolizing binder until they reach a temperature comparable to the propellant burning surface temperature (at which time they are in a layer of partially decomposed, molten binder).

When the aluminum particles melt, they expand visibly and tend towards a spherical shape (if not already spherical). This suggests that the oxide shell will stretch, fracture or exude aluminum through pores, as the expansion of the aluminum must be accomodated. Results to date do not establish the mode of oxide breakdown, but observations of cracking, wart formation and drainage of aluminum from the shells establish that the breakdown is varied in nature, dependent on routine differences in oxide, and dependent on presence or absence of an oxidizing atmosphere to limit the flow of escaping aluminum (by forming a constraining oxide surface).

In propellant combustion, these details of behavior are important because both ignition and agglomeration are controlled by the nature of the breakdown of the oxide barrier on the aluminum surface. In this respect, ignorance of the mechanical properties of the oxide shell at high temperature continues to impede rationalization of experimental observations of the detailed behavior, and the effect of variables related to the oxide skin.

Accumulate Formation

Retention of aluminum particles on the burning surface is synonymous with accumulation, which is observed to be extensive. The presence of molten binder residues to high temperatures assures that the accumulating particles will adhere as they concentrate and continue to adhere until heated to quite high temperatures (e.g., up to 1000°C with HTPB binder). The present results with aluminum-loaded binder samples support this. Further, the results indicate that the particles may adhere to each other even under conditions where adhesion by binder breaks down. Tests on aluminum powder confirmed the concept of direct sintering of particles, and showed it to follow from the breakdown of the oxide shells. The correlation among observations of oxide shell break down, particle interactions (sintering), and earlier propellant combustion observations (vs. type of aluminum) indicates that the direct particle interactions are of comparable importance to binder adhesion in the "life cycle" of aluminum accumulates in the combustion zone. This correlation is important to any efforts to predict or control aluminum behavior, and will be studied more fully in future work by study of accumulates formed in combustion of model propellants.

Agglomeration

The culmination of all the behavior of aluminum on the burning surface is the coalescence of the aluminum particles in the accumulates, and the concurrent ignition. This reflects the final breakdown of the oxide shells and the dominance of surface tension in aluminum, producing "agglomerates". Laboratory heating tests are useful in studying agglomeration because the process can be observed in detail; can be run conveniently with and without binder and/or oxidizing species; and can be interrupted short of ignition, to permit post-test examination of samples. In such tests, different powders agglomerate differently, apparently because of different characteristics of the oxide shells. Consistent with this, agglomeration is less rapid and less complete in oxidizing atmospheres (oxygen), where escape of molten aluminum is impeded by formation of new solid oxide on fresh aluminum surface. Agglomeration occurs in tests on aluminum-loaded binder, but less extensively than in the absence of binder, implying that binder products continue to impede particle contact to some extent to temperatures up to 1000°C. Post-test studies of agglomerates suggest the manner of their formation by breakdown of oxide shells and surface tension-induced flow of aluminum.

The present observations of agglomeration are generally consistent with earlier ones (Ref. 1), and amplify on them relative to the role of binder and the role of heating rate (hot plate drop tests). This improves the relevance of all prior work to combustion zone behavior, and shows a useful comparability between heating experiments and combustion zone behavior. However, there are many aspects of the combustion zone behavior that cannot be simulated by heating experiments. It is important to get on to the unresolved issues of: condition and size of agglomerates, surface residence of agglomerates, ignition, and burning while on the surface; dependence of these attributes and processes on propellant and environmental variables; and dominant mechanistic basis and control of these processes in the rapid heating situation of the combustion zone.

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GLOSSARY

Agglomerate (noun) -- a collection of two or more particles that have run together to such an extent that the original particles are no longer distinguishable.

Al -- aluminum.

AlMP -- melting point of aluminum.

AP -- ammonium perchlorate.

Ar -- argon.

Chains -- sequence of interconnected original particles, sometimes branching.

Coating -- refers to the layer of oxide on the aluminum particles or agglomerates.

Cracking -- an appearance that the oxide coating on a particle had split open and allowed molten aluminum to escape: some uncertainty as to actual cause of this appearance.

CTPB -- carboxy terminated polybutadiene (binder)

Densely packed -- refers to a powder sample spread on the hot plate densely enough so that the array is two or three particles deep.

Dispersed -- refers to a powder sample spread on the hot plate so thinly that 50% or so of the particles do not touch each other.

Extensive -- 50% or so of particles involved.

HPD -- hot plate drop.

HSM -- hot stage microscope.

HTPB -- hydroxy terminated polybutadiene (binder)

Moderate -- 20 - 30% of particles involved.

Oxidative Welding -- a particular sintering process involving bridging between particles with aluminum and oxidation of the aluminum in place.

PBAA -- polybutadiene-acrylic acid (binder)

PS -- polysulfide (binder)

SEM -- scanning electron microscope.

Shell -- same meaning as "coating", but used in the context of remnants after drainage of aluminum.

Sinter -- particles stick together by means of particle interaction (rather than an adhesive agent).

Skin -- same meaning as "coating", but used in the context of a coating with mechanical properties.

Slight -- easy to find but doesn't involve many of the particles.

Sparsely packed -- same as "dispersed".

Trace -- can find if look hard.

Warts -- protrusions on particles that appear to be formed by expulsion of aluminum through flaws in the oxide coating due to expansion during heating.

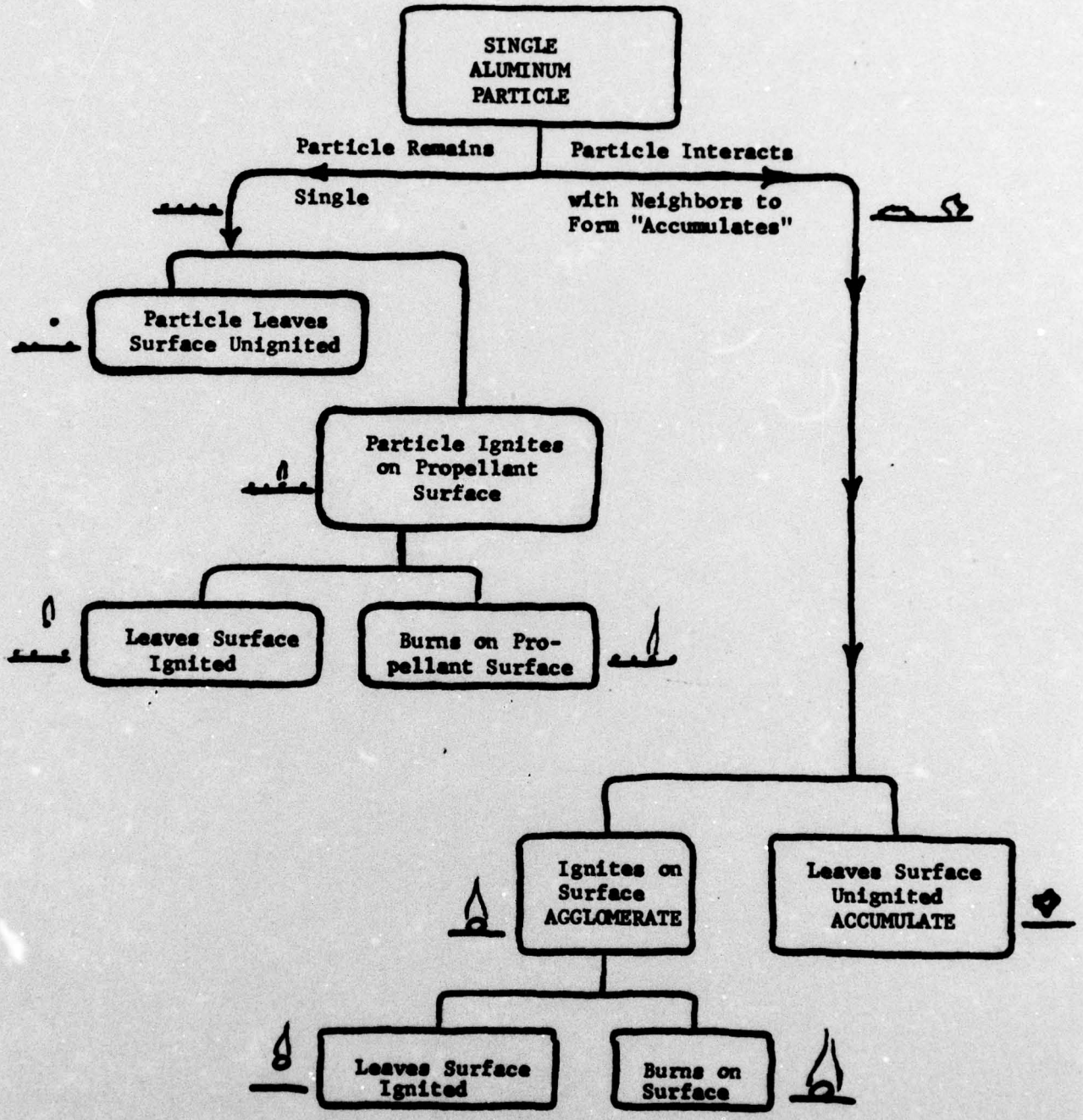


Figure 1. Sequences of behavior of aluminum on a propellant burning surface.

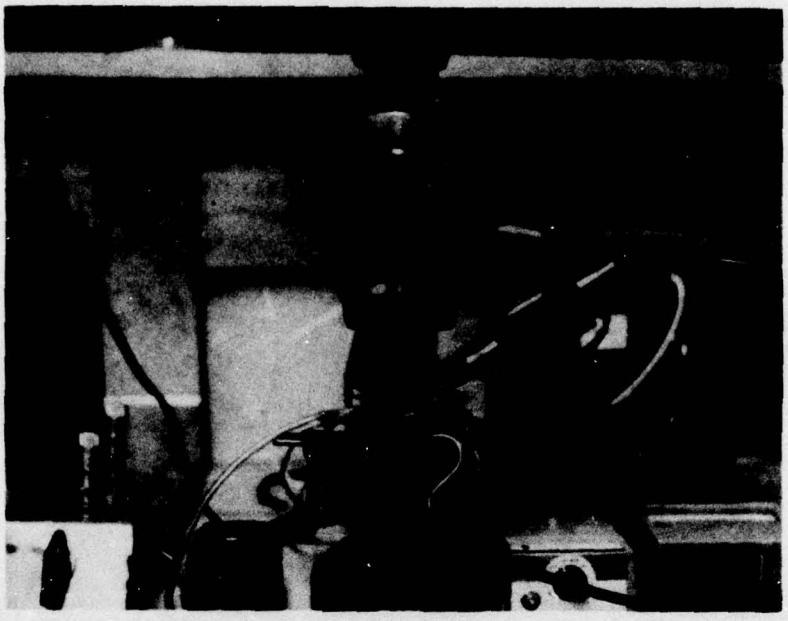
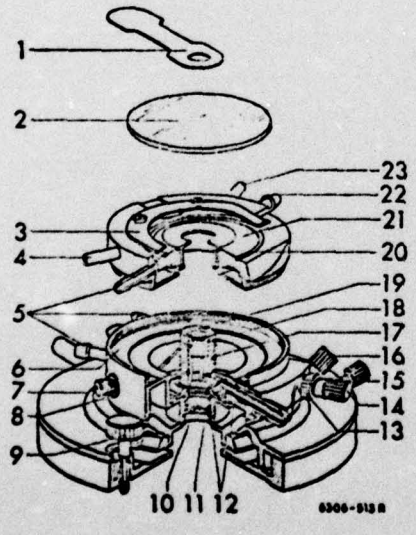


Figure 2. Arrangement for the Hot Stage Microscope Experiments.



1. Spoon diaphragm stop
2. Quartz plate
3. Leaf spring
4. Protective gas socket
5. Sockets for cooling water
6. Rubber ring
7. Current connection
8. Round cord ring
9. Clamping screw
10. Quartz plate
11. Clamping ring
12. Round cord ring
13. Milled nut for the thermo-element
14. Connection "Measuring instrument"
15. Milled screw for orientating the object
16. Milled screw for the horizontal alignment of the object
17. Heating cartridge
18. Object carrier support with thermo-element
19. Object carrier
20. Round cord ring
21. Diaphragm stop
22. Socket for cooling water
23. Socket for protective gas

Figure 3. Detailed View of the Microscope Hot Stage (figure from the manufacturer's brochure).

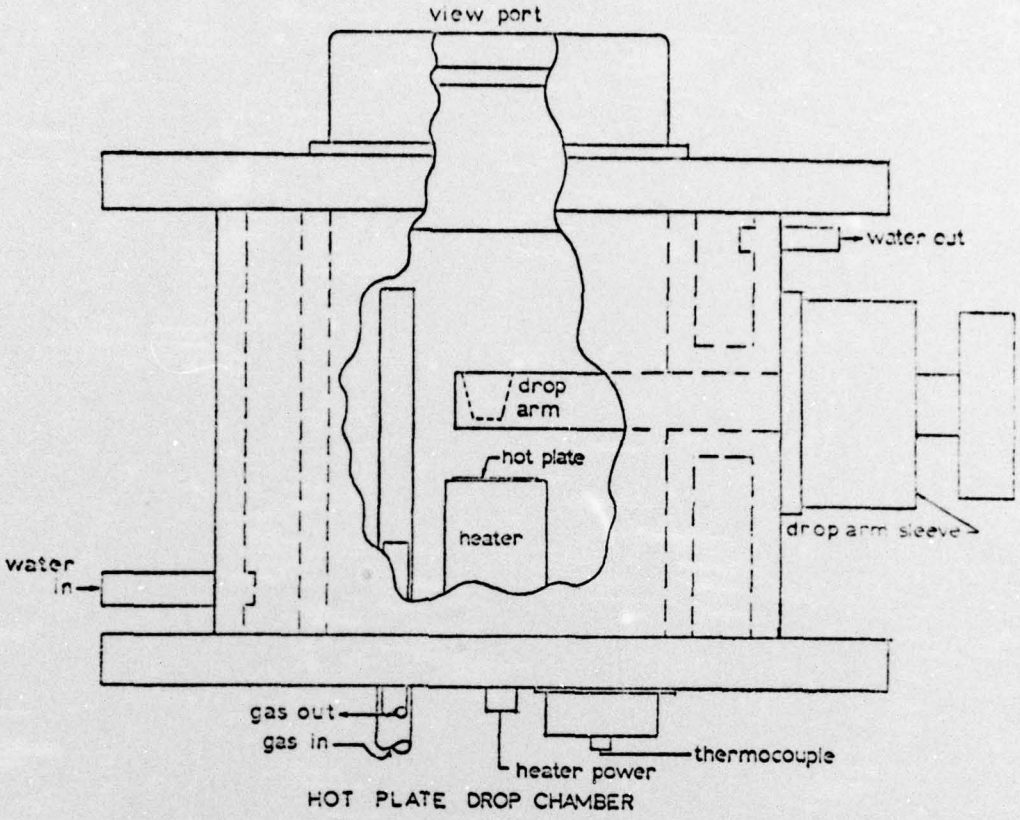


Figure 4. Details of the Hot Plate Drop Test Apparatus

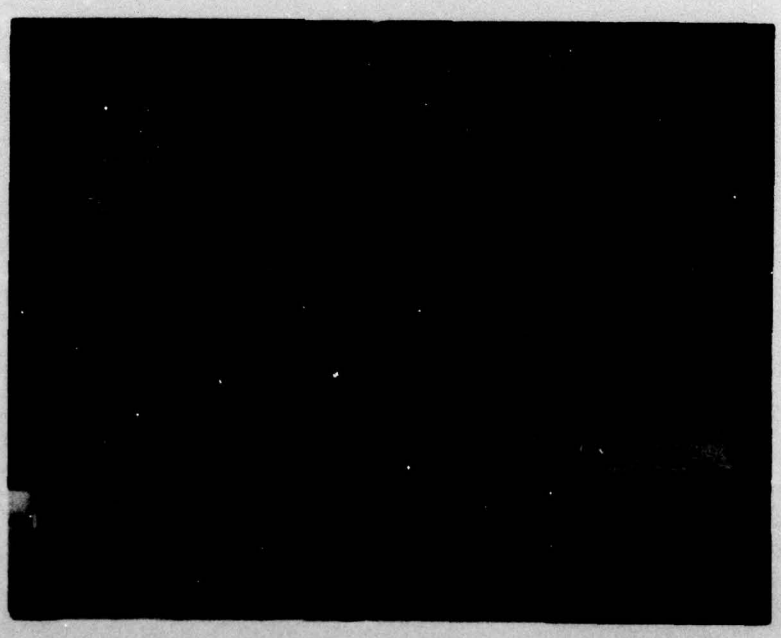
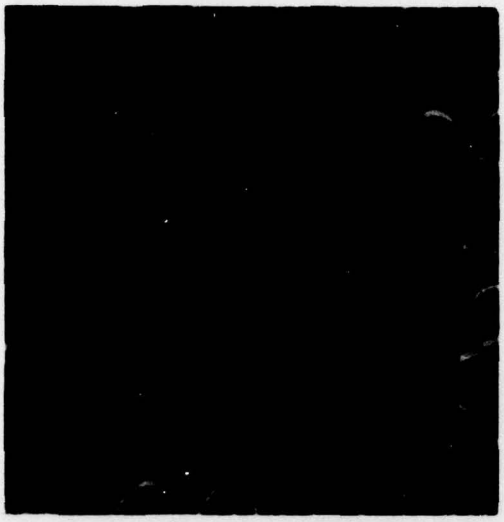
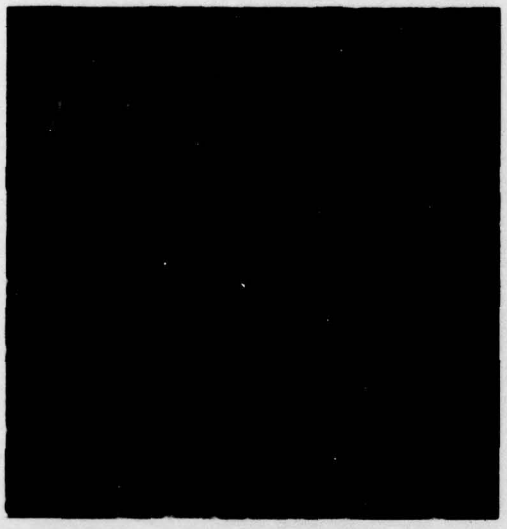


Figure 5. Hot Plate Drop Test Apparatus.

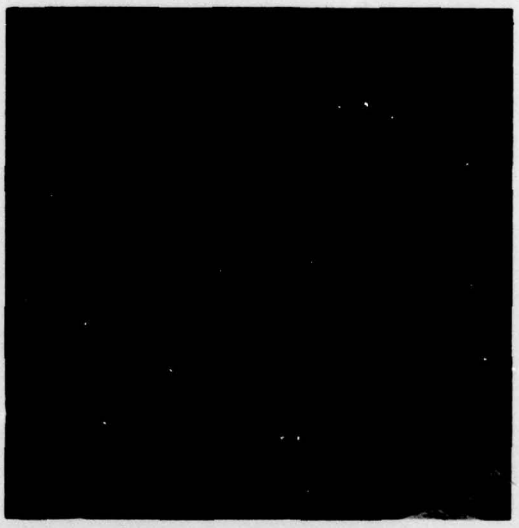


H-30

Alcoa 123

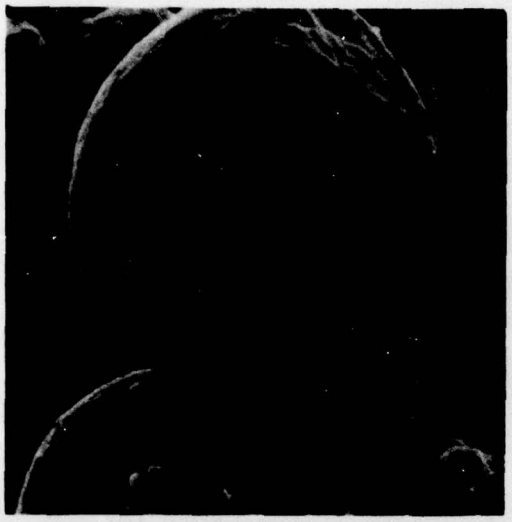


Modified H-30

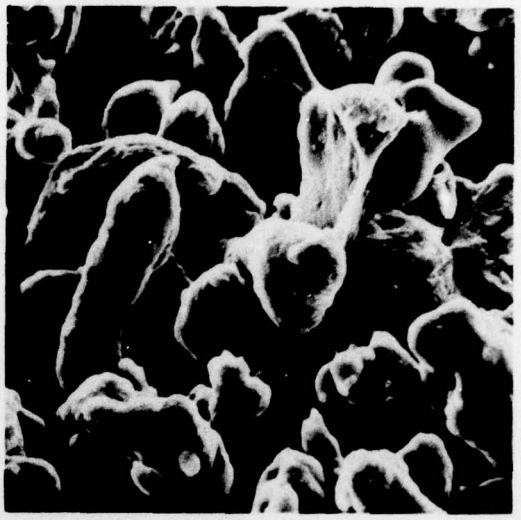


H-95

Figure 6a. Scanning Electron Micrographs of the Four Aluminum Powders Most Extensively Tested - General Shape (200x).

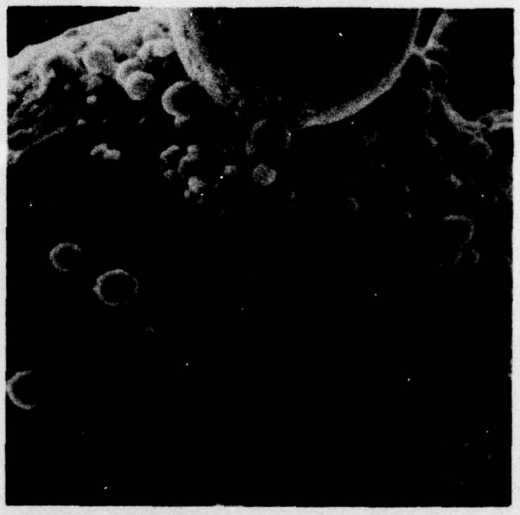


H-30



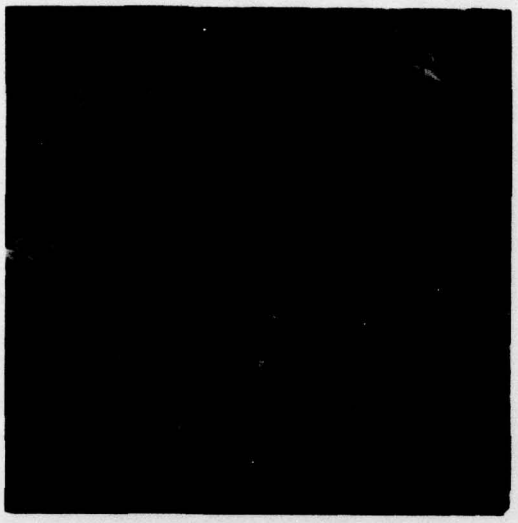
Alcoa 123

Modified H-30

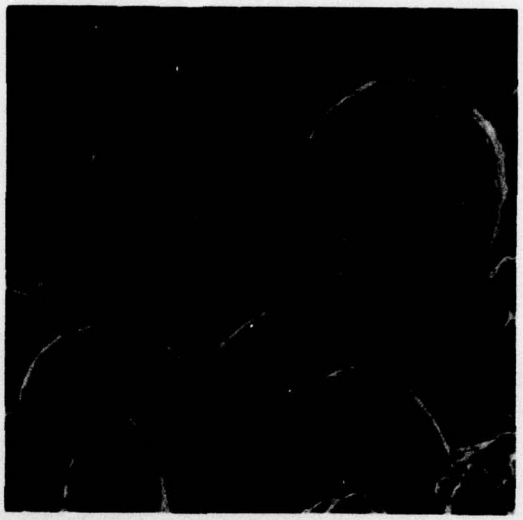


H-95

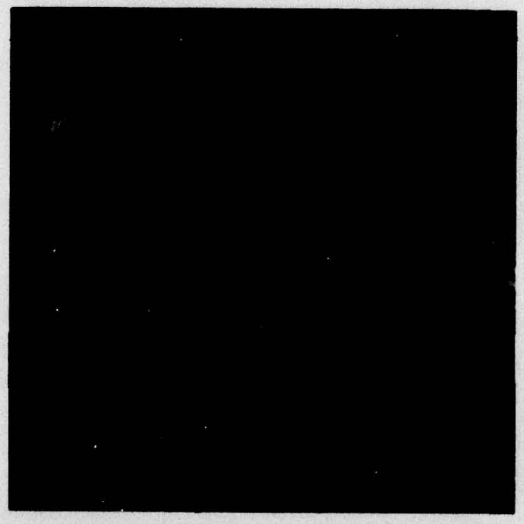
Figure 6b. Scanning Electron Micrographs of the Four Aluminum Powders Most Extensively Tested - Surface Details (1000x).



a) Untreated (1000x)

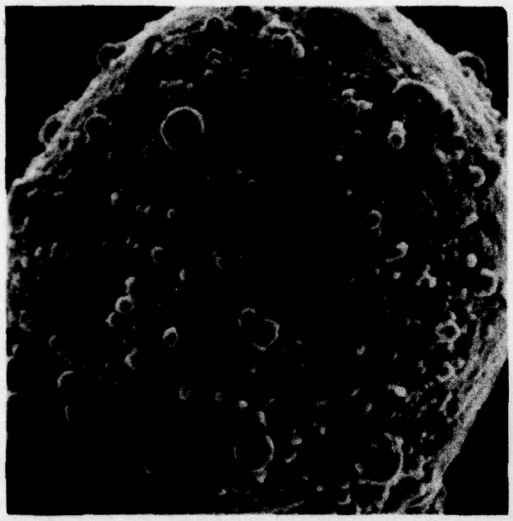


b) 10% HCl for 10 min (500x)

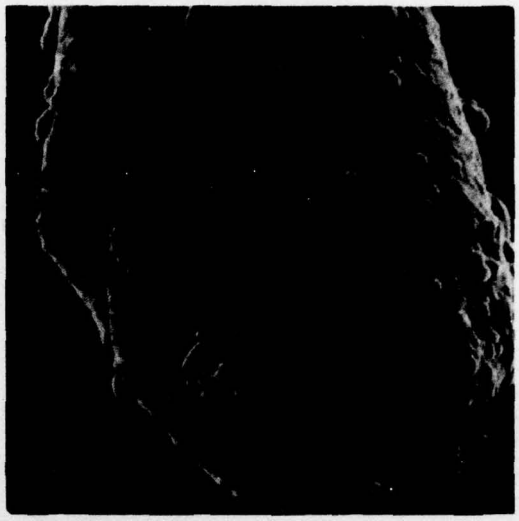


c) 100% HCl for 10 min (1000x)

Figure 7. Effect of Acid Treatment on H-30 Aluminum.

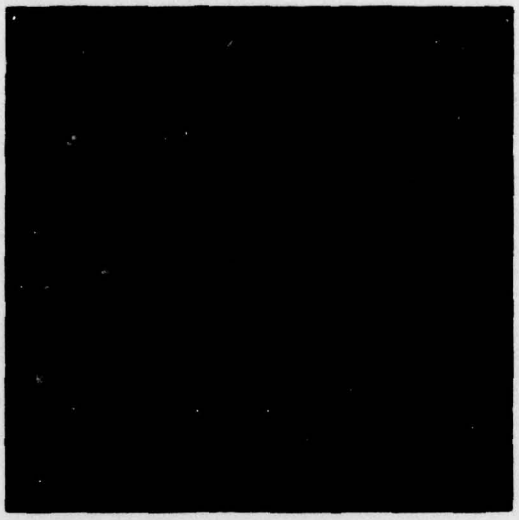


a) Untreated (500x)



b) 10% HCl for 10 min (500x)

c) 50% HCl for 5 min (500x)



d) 50% HCl for 5 min (2000x)

Figure 8. Effect of Acid Treatment on H-95 Aluminum.

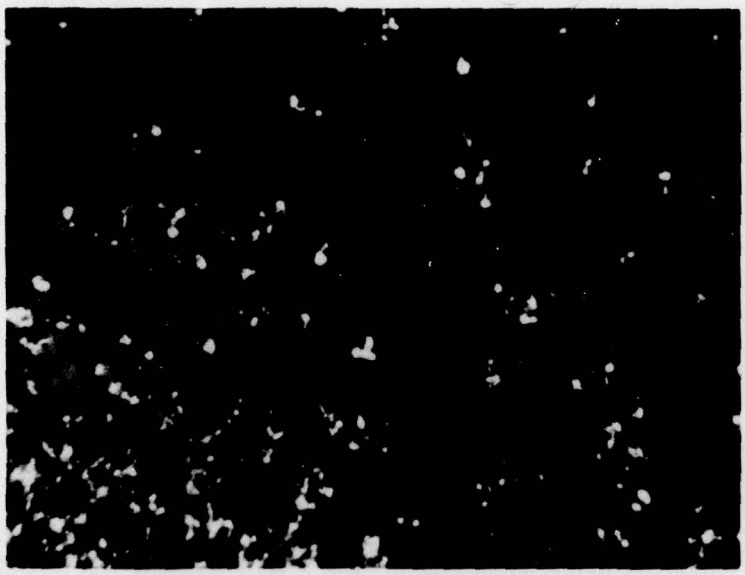


Figure 9. Illustration of Strings or Chains of Aluminum Formed During Heating (H-30 Aluminum Heated in O_2 to 800°C: magnification 80x).

Figure 10. Example of Warts Formed During Heating (H-30 Aluminum Heated in Argon to 760°C: magnification 1700x).

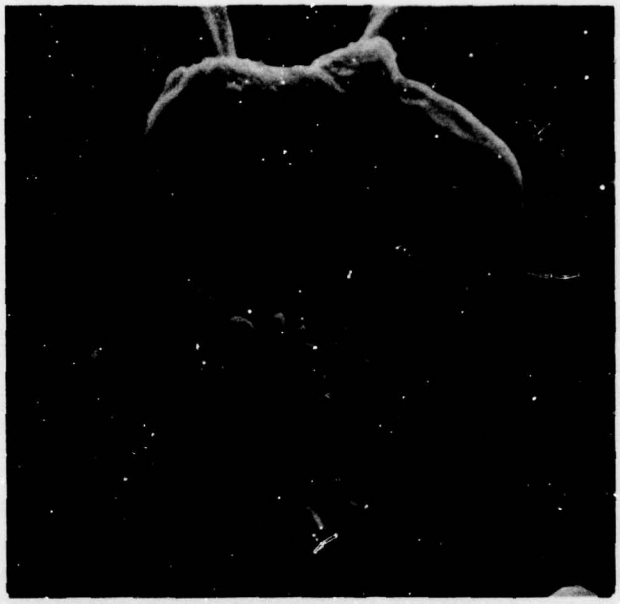


Figure 11. Bridging Between Two Aluminum Particles During Heating (H-30 Aluminum Heated in Argon to 1000°C: magnification 2200x).

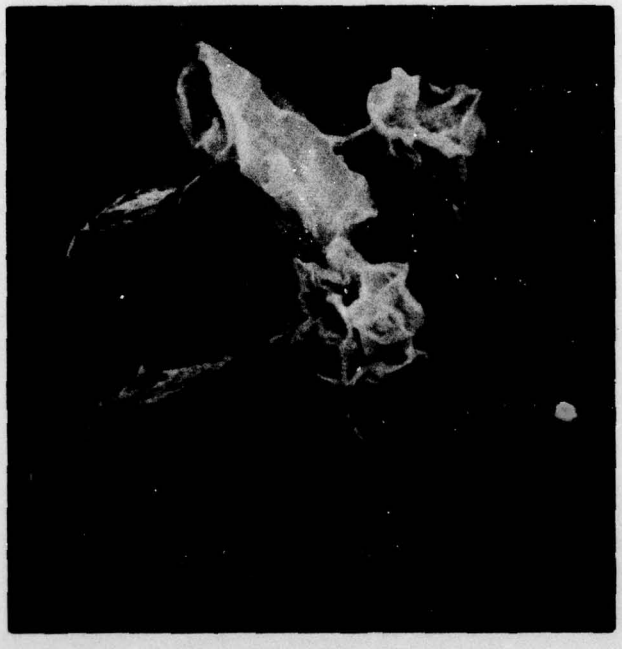
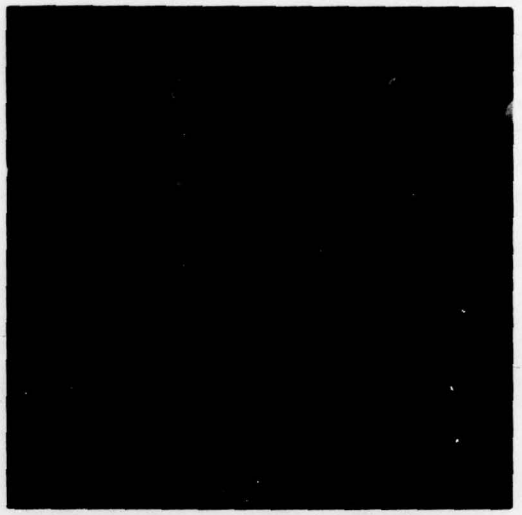


Figure 12. Drainage of Aluminum from the Oxide Skin on a Platinum Surface. The cones looked the same when formed on the side of the wire. (H-30 Aluminum heated in Oxygen to 1000°C: magnification 1600x).

H-30 heated to 760°C in Ar
(1800x)



Alcoa 123 heated to 1000°C in Ar
(550x)

H-30 heated to 1000°C in Ar
(2000x)

H-30 heated to 1000°C in Ar
(5000x)

Figure 13. Examples of Drainage of Aluminum Particles on Platinum Wire During Heating.

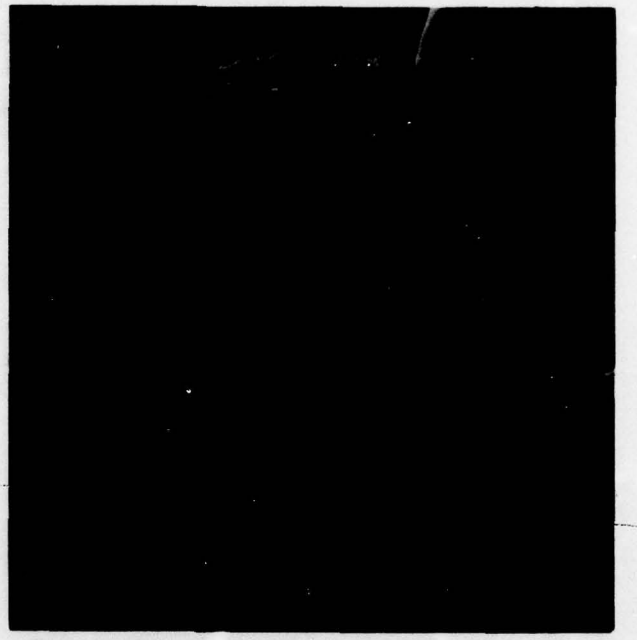
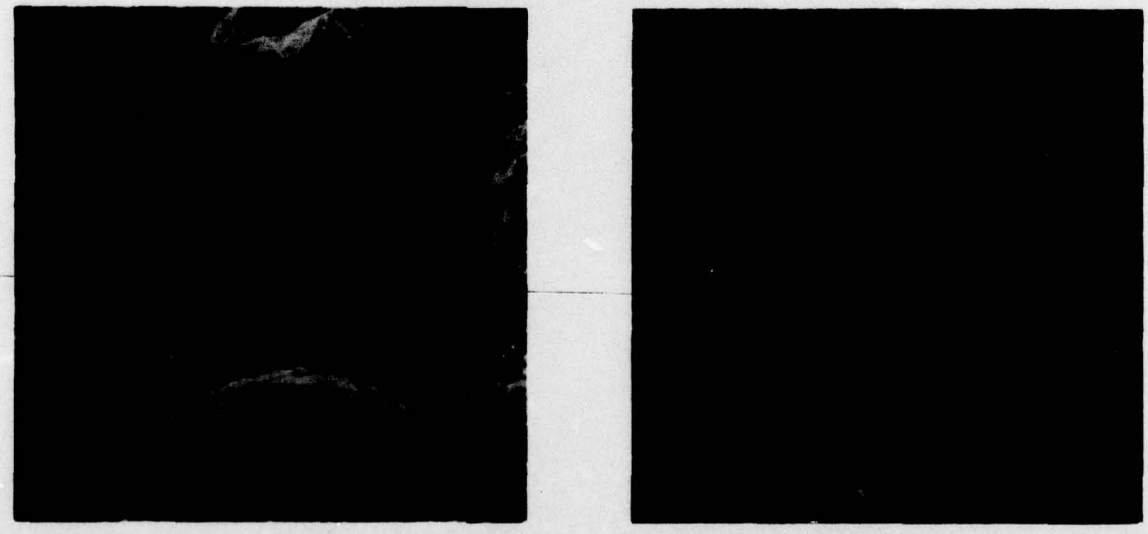


Figure 14. Drainage of Modified H-30 Particles on Platinum Wire (compare with Figure 13; note less decisive drainage of particles).



Argon Oxygen

Figure 15. Comparison of Agglomeration in Argon and in Oxygen.

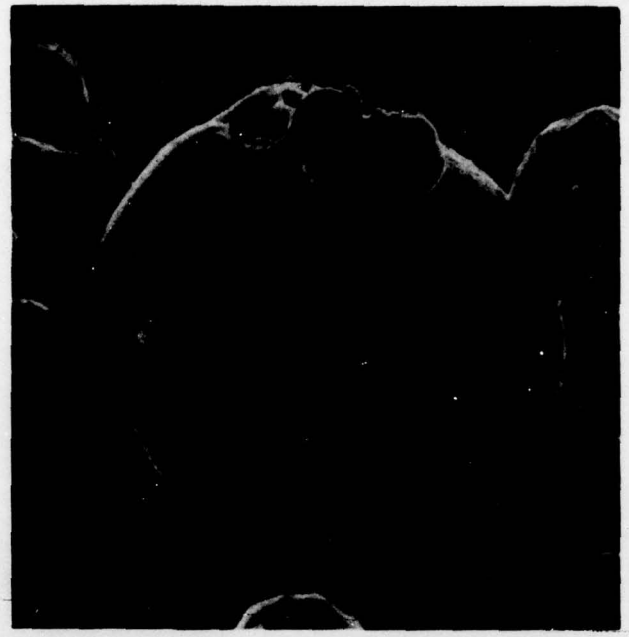
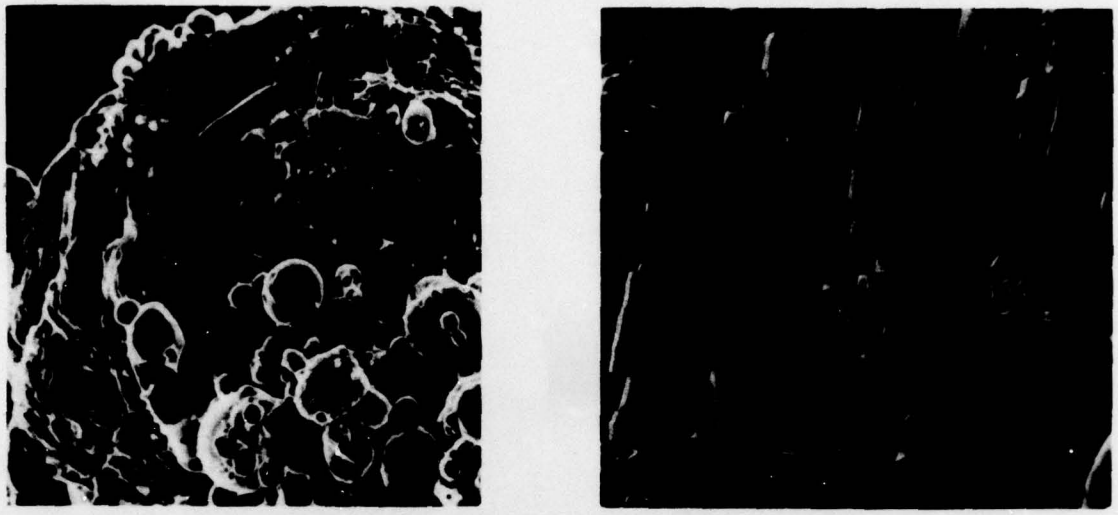


Figure 16. An Agglomerate that Has Not Yet Spherodized, still showing evidence of the constituent particles (H-30 Aluminum, heated to 700°C in Air: magnification 1000x).

Figure 17. A Spherical Agglomerate, typical of tests to 1000°C (H-30 Aluminum, heated to 1000°C in Argon: magnification 200x).



(200x) (1000x)

Figure 18. An Agglomerate that Has Been Etched for 5 Minutes in 50% HCl (H-30 Aluminum, heated to 1000°C in Air).

Figure 19. Array of Interconnected Aluminum Particles that Remain After Heating an Aluminum-Loaded Binder Sample, Showing Evidence of the Bubbling Activity of the Binder during Heat-up (H-30 Aluminum in CTPB Binder, O_2 Atmosphere, HPD test), Magnification 100x.

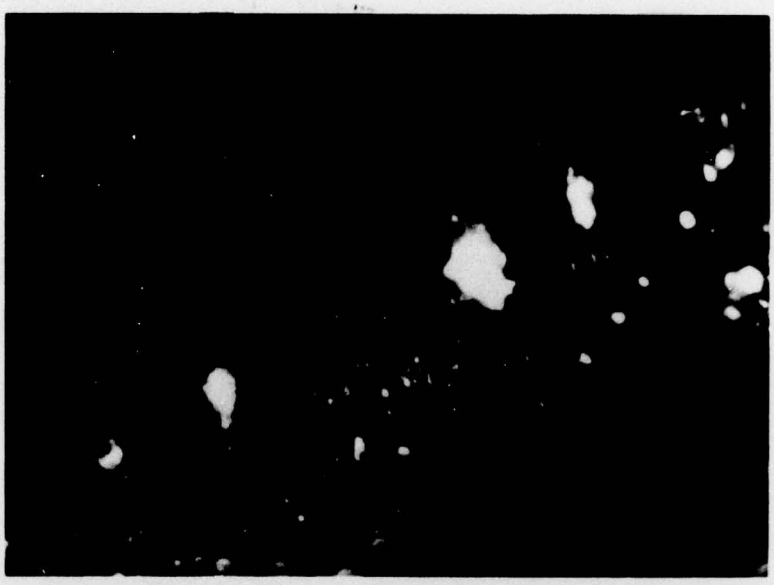


Figure 20. Aluminum "Whiskers" Formed on Agglomerate During Hot Plate Drop Tests, apparently due to drawing out of adhering aluminum during shrinkage of samples (H-30 Aluminum in CTPB Binder, O_2 Atmosphere, HPD test: magnification

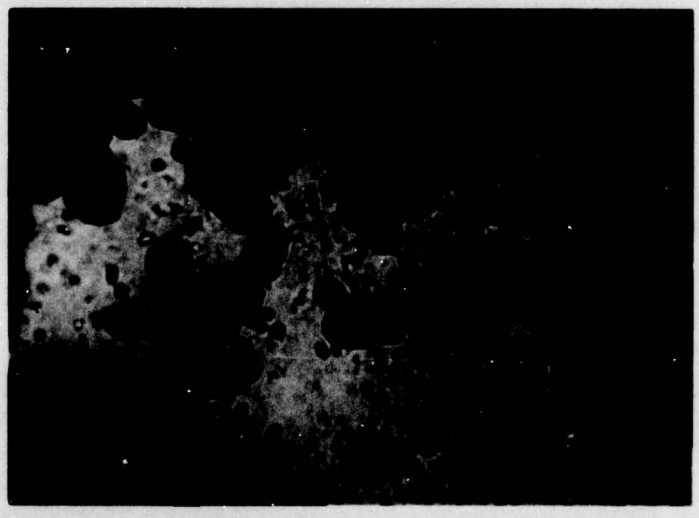


Figure 21. Hot Plate Drop Test Sample Shoring Some Empty Oxide Shells (Modified H-30 Aluminum in CTPB Binder, Air atmosphere: back lighted optical microscope picture; magnification 200x).